

# The Reaction of LiD with Moisture by Temperature Programmed Reaction (TPR)

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# **The reaction of LiD with moisture by Temperature Programmed Reaction (TPR)**

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## **ABSTRACT**

The temperature programmed reaction technique was performed on LiOH powders and LiD single crystals previously exposed to different moisture levels. Our results show that the LiOH decomposition process has an activation energy barrier of 30 to 33.1 kcal/mol. The LiOH structure is stable at 320 K for 100 years. However, LiOH structures formed on the surface of LiD during moisture exposure at low dosages may have multiple activation energy barriers, some of which may be much lower than 30 kcal/mol. We attribute the lowering of the activation energy barrier for the LiOH decomposition to the existence of dangling bonds, cracks, and other long range disorders in the LiOH structures formed at low levels of moisture exposure. These defective LiOH structures may decompose significantly over the next 100 years of storage even at room temperature. At high moisture exposure levels, LiOH.H<sub>2</sub>O formation is observed. The release of H<sub>2</sub>O molecules from LiOH.H<sub>2</sub>O structure has small activation energy barriers in the range of 13.8 kcal/mol to 16.0 kcal/mol. The loosely bonded H<sub>2</sub>O molecules in the LiOH.H<sub>2</sub>O structure can be easily pumped away at room temperature in a reasonable amount of time. Our experiments also suggest that handling LiD single crystals at an elevated temperature of 340 K or more reduces the growth of LiOH and LiOH.H<sub>2</sub>O significantly.

## **I. INTRODUCTION**

As a result of exposure to water vapor during routine handling, a corrosion layer will form on the surface of lithium deuteride. It is believed that, depending on the conditions of exposure, LiOH and/or Li<sub>2</sub>O are formed with some LiOH.H<sub>2</sub>O formation at higher exposure levels. In order to better understand the LiD and H<sub>2</sub>O interaction, temperature programmed reaction (TPR) experiments have been conducted on LiOH powders and LiD single crystals under a variety of environmental conditions. The activation energies have been determined over a range of H<sub>2</sub>O exposure levels.

## **II. EXPERIMENTS**

LiOH powders were prepared by reacting LiD powders in a beaker containing liquid H<sub>2</sub>O over many days. Water was allowed to evaporate at room temperature, leaving the powders behind. The powders were then wrapped inside a Pt envelope. The side of the envelope facing a quadrupole mass-spectrometer was perforated with many holes over the entire surface.<sup>1</sup> The loaded foil was held fixed to a sample holder by way of three mechanical clamps and transferred into an ultrahigh vacuum (UHV) chamber with a base pressure of 10<sup>-6</sup> Pa (4 x 10<sup>-7</sup> Pa in the detector chamber) through a differentially pumped load lock. The sample was pumped in the UHV chamber for a few hours to remove H<sub>2</sub>O molecules that were loosely bonded to the powders. A type K thermocouple was inserted between the Pt envelope surface and a clamp holding the envelope for temperature measurement. The samples were heated by passing currents through a Tungsten coil located 2 mm behind the samples.

Some LiD single crystals were cleaved in air, then exposed to ambient air for a certain length of time prior to TPR experiment. Others were cleaved in a glove bag which was attached directly to the entrance port of the TPR load chamber and back-filled with N<sub>2</sub> (10 to 20 % relative

humidity). The samples, which had been cleaved in the glove bag, were also heat-treated at a predetermined temperature for a given length of time, cooled down to room temperature, then exposed to a studied level of moisture for a planned amount of time. All samples were pumped from a few hours to a few days prior to TPR experiment.

### III. RESULTS & DISCUSSION

Fig. 1 shows the H<sub>2</sub>O TPR signals from LiOH powders and the corresponding Arrhenius plot near the TPR onset.

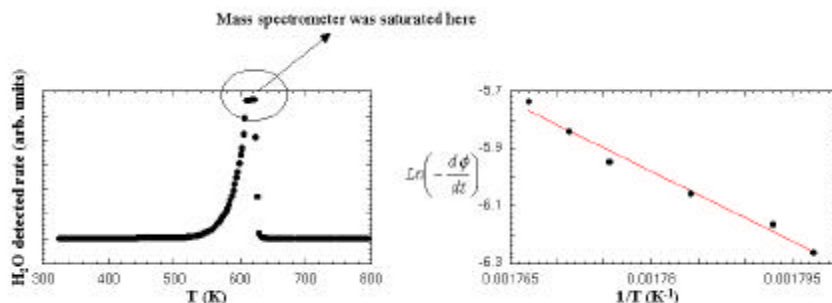


Fig. 1: H<sub>2</sub>O TPR signals from LiOH powders and the corresponding Arrhenius plot near the TPR onset

Here,  $\phi$  (unitless) represents the ratio of the number of LiOH molecules at time  $t$  over the initial number of LiOH molecules before the start of the TPR process. There was only one decomposition energy site at around 620 K. The activation energy of decomposition of LiOH is determined, by plotting  $\ln[-d(\ln\phi)/dt]$  vs.  $1/T$  near the TPR onset, to be in the range of 30 kcal/mol to 32.2 kcal/mol. The pre-exponential factor is on the order of  $9.0 \times 10^8 \text{ s}^{-1}$  to  $8.5 \times 10^9 \text{ s}^{-1}$ . The kinetic reaction order  $n$  is between 0.5 and 0.75. The fact that the kinetic reaction order  $n$  for the LiOH decomposition process is not 2 suggests that the reaction  $2\text{LiOH} \Rightarrow \text{Li}_2\text{O} + \text{H}_2\text{O}$  in LiOH powders is not an elementary process. With an activation energy for the decomposition of 30 to 32 kcal/mol and a pre-exponential factor on the order of  $9.0 \times 10^8 \text{ s}^{-1}$  to  $8.5 \times 10^9 \text{ s}^{-1}$ , LiOH is very stable at room temperature.

Fig. 2 shows the TPR spectra of a LiD single crystal previously exposed to ambient air for 2 hours.

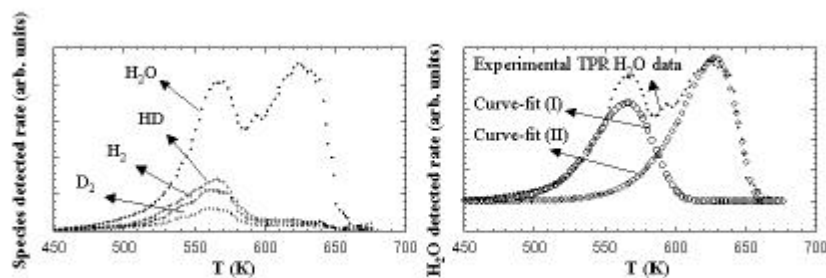


Fig. 2: TPR data from a single crystal LiD previously exposed ambient air for 2 hours .

Unfortunately, due to experimental difficulty with the heating system below 450 K, only data in the 450K to 700 K is presented here. The TPR data reveal that the decomposition of LiOH into Li<sub>2</sub>O and H<sub>2</sub>O has multiple activation energy barriers between 450 K to 700 K. The technique of iteration regression analysis yields two separate decomposition curves: (I)  $n \approx 1$ ,  $E = 26$  to 29.7

kcal/mol,  $\nu = 1.53 \times 10^8$  to  $5.95 \times 10^9 \text{ s}^{-1}$  and (II)  $n \approx 0.75$ ,  $E = 30.5$  to  $33.1$  kcal/mol,  $\nu = 7.72 \times 10^8$  to  $6.41 \times 10^9 \text{ s}^{-1}$ .<sup>2</sup> The decomposition curve (I) has a smaller activation energy barrier and is attributed to the decomposition of LiOH structures with a lot of defects such as dangling bonds, cracks, and other long range disorders. The decomposition curve (II) has a higher activation energy barrier and is attributed to the decomposition of LiOH structures with less defects. It is noted from Fig. 2 that the amounts of HD, H<sub>2</sub>, and D<sub>2</sub> detected were only a fraction of the amount of H<sub>2</sub>O detected. They also evolved most heavily near the region of decomposition dominated by LiOH structures with more defects. This suggests that there are more defects in the LiOH structure near the LiD/Li<sub>2</sub>O/LiOH interface where stress due to lattice mismatches is most pronounced. With a smaller activation energy barrier, LiOH structures with a lot of defects may decompose significantly over the next 100 years of storage at 320 K. Fig. 3 shows the simulated decomposition of two LiOH structures: one with less defects (30.5 kcal/mol) and one with more defects (26 kcal/mol) at 300 K and 320 K. As in the case of LiOH powders, the LiOH structure with  $E = 30.5$  kcal/mol decomposes minimally over 100 years, however, about 60 % of the more defective LiOH structure with  $E = 26$  kcal/mol decomposes in the same time span at 320 K.

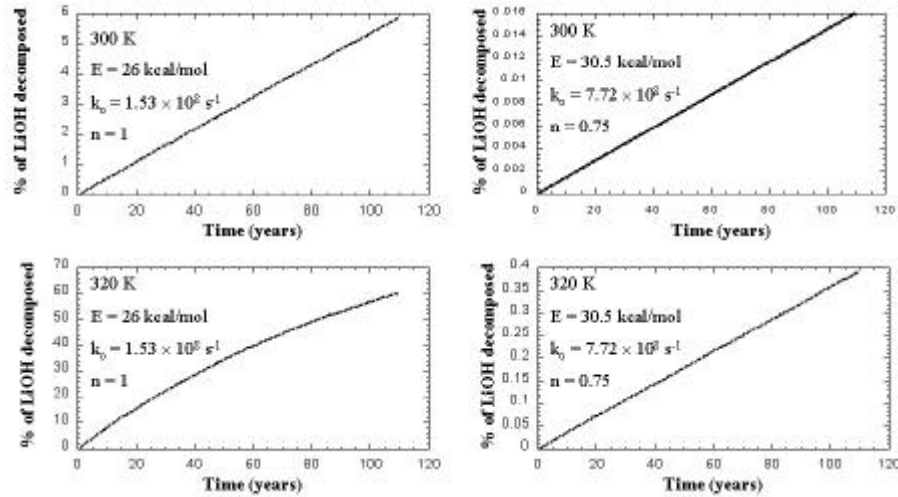


Fig. 3: Simulations of the decomposition of two LiOH structures: one with less defects (30.5 kcal/mol) and one with more defects (26 kcal/mol) at 300 K and 320 K.

In another TPR experiment of a LiD single crystal previously exposed to ambient air for 8 minutes at an approximately 30% to 40 % relative humidity, we have successfully obtained TPR data in the temperature window of 300 K to 450 K. There were 2 desorption sites in this window corresponding to the decomposition of LiOH.H<sub>2</sub>O structures at energies of 13.8 to 14.6 kcal/mol and 14.9 to 16 kcal/mol with corresponding pre-exponential factors of  $7.45 \times 10^6$  to  $2.43 \times 10^7 \text{ s}^{-1}$  and  $1.96 \times 10^6$  to  $7.47 \times 10^6 \text{ s}^{-1}$ . The loosely bonded H<sub>2</sub>O molecules in the LiOH.H<sub>2</sub>O structure can be easily pumped away at room temperature in a matter of hours.<sup>2</sup>

In the following set of experiments (Fig. 4), a LiD single crystal, which had been annealed to 503 K for 48 hours in an ultrahigh vacuum environment and then cooled down to room temperature, was exposed to 39 ppm of moisture for 4 hours prior to TPD experiment. After that, the same sample was subjected to the same heating and cooling cycle described above, then exposed to 399 ppm of moisture for 3.2 hours prior to TPD experiment. A similar heating and cooling cycle was applied to the sample before it was exposed once again to moisture at 779 ppm for 20 hours. The upper part of Fig. 4 shows the TPR spectra of this sample after three separate moisture exposures. It is noted that as the level of water exposure increased, the first TPR peak

shifted to higher temperature, implying an increase in the activation energy of decomposition of LiOH. In the lower part of Fig. 4, we show the Arrhenius plot for the determination of the activation energy of decomposition in the three cases. It is seen, here, that the lower levels of moisture exposure formed "poor quality" LiOH which decomposed at lower temperatures than the "good quality" LiOH formed at higher levels of moisture exposure. In the Arrhenius plots,  $\Gamma_{H_2O}$  designates the flux of  $H_2O$  detected by the mass-spectrometer. So, in general, we observe that at lower exposure dosages, the LiOH formation is highly defective and has components which tend to decompose at much lower activation energy barrier than 30 kcal/mol.

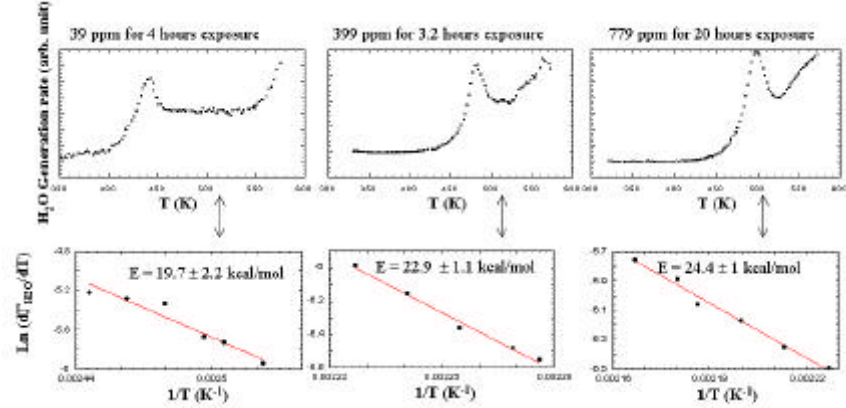


Fig. 4:  $H_2O$  TPR spectra of a LiD single crystals after three separate moisture exposures and the corresponding Arrhenius plots for the determination of the activation energies of decomposition.

In Fig. 5, we show qualitatively the different growth paths for LiOH on LiD single crystals as a function of moisture exposure.

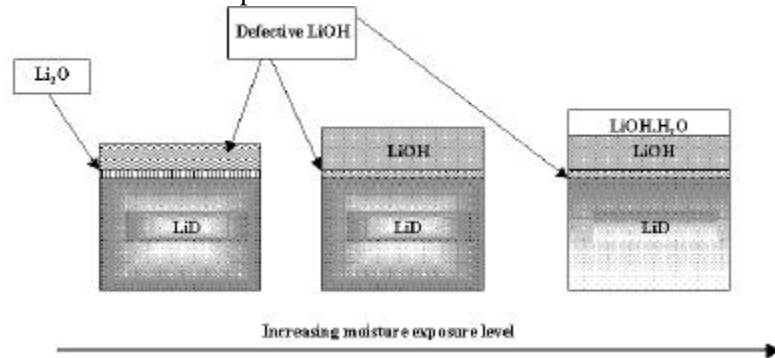


Fig. 5: Growth paths for LiOH on LiD as a function of moisture exposure levels

It is seen from this figure that as a result of long exposure in a moist environment, one can grow stoichiometric  $LiOH.H_2O$  or LiOH on LiD single crystals. There would always be some defective LiOH structures near the LiOH/LiD interface, however, due to lattice mismatch induced stress there. In a dry environment with residue moisture on the order of a few ppm, LiOH structures with dangling bonds, cracks, and other long range disorders are predominant, even far away from the LiOH/ $Li_2O$ /LiD interface. Note that in a vacuum or dry environment, due to a lack of supply of  $H_2O$  molecules to the LiOH/LiD interface, LiD reacts with LiOH to form  $Li_2O$  and hydrogen species instantaneously at the interface and hence the formation of LiD/ $Li_2O$ /LiOH interface.

Fig. 6 shows that the reaction of LiD with moisture is significantly reduced at elevated temperatures, even at atmospheric pressures with 50 % relative humidity. From the left image, it is seen that at 50 % relative humidity, air exposure of a LiD single crystal for 30 hours at  $T = 300$  K resulted in  $\sim 30$   $\mu\text{m}$  thick of reacted layer (LiOH and/or  $\text{LiOH}\cdot\text{H}_2\text{O}$ ). The samples presented in the left and the right images of Fig. 6 were originally from the same LiD single crystal which was subsequently cleaved into two smaller pieces. The sample on the right of Fig. 4 was subjected to the same moisture exposure conditions as the one on the left, except at a slightly elevated temperature of  $T = 339$  K. The reacted layer from right sample was less than  $6$   $\mu\text{m}$ !

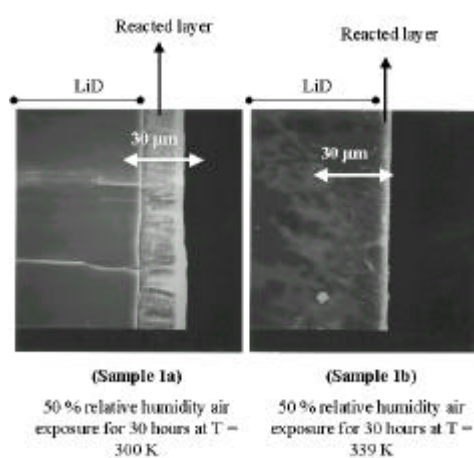


Fig. 6: The reaction of LiD with moisture is greatly reduced at elevated temperatures as measured by SEM.

#### **IV. CONCLUSION & DISCUSSION**

We have performed TPR on LiOH powders and LiD single crystals previously exposed to different moisture levels. Our results show that the decomposition process of LiOH has a high activation energy barrier of between 30 kcal/mol and 33.1 kcal/mol. The LiOH structure is stable even if kept at an elevated temperature of 320 K for 100 years. However, LiOH structures formed at low levels of moisture exposure may have an activation energy barrier much lower than 30 kcal/mol. We attribute the low activation energy barriers for the decomposition of these LiOH structures formed at low levels of moisture exposure to the existence of dangling bonds, cracks, and other long range disorders in the LiOH structures. These defective LiOH structures may decompose significantly over the next 100 years of storage even at room temperature. We are currently in the process of quantifying the ratios of bad quality LiOH to good quality LiOH under a variety of moisture exposure levels. At high moisture exposure levels, the release of  $\text{H}_2\text{O}$  molecules from  $\text{LiOH}\cdot\text{H}_2\text{O}$  structure has a small activation energy barrier of between 13.8 kcal/mol to 16.0 kcal/mol. The loosely bonded  $\text{H}_2\text{O}$  molecules can be easily pumped away at room temperature in a reasonable amount of time. Our experiments also suggest that handling LiD at an elevated temperature  $\geq 340$  K efficiently reduces the growth of LiOH and  $\text{LiOH}\cdot\text{H}_2\text{O}$ .

#### **V. ACKNOWLEDGEMENT**

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2. Interested readers are referred to a more detailed report to be published at Lawrence Livermore National Laboratory by the same authors of this paper at a later time.